



Photopolymerization kinetics of α -disulfone cationic photoinitiator

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ABSTRACT

An α -disulfone cationic photoinitiator called 4-tolyl methyl disulfone was synthesized and characterized by UV–vis absorption spectroscopy, LCMS, IR and NMR. Eight vinyl ether monomers were chosen to study the kinetics of photopolymerization by real-time infrared spectroscopy (FT-IR). It showed that 4-tolyl methyl disulfone was an effective cationic photoinitiator. The rate of polymerization and ultimate conversion increased with increase of 4-tolyl methyl disulfone concentration and light intensity.

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1. Introduction

Current and future importance of UV curing can be hardly overstated. The rapid adoption of UV curing and a myriad of uses in industry promoted rapid development in this field. The various applications included coatings, adhesives, inks and advanced high technology uses such as microelectronic encapsulation, photo- and stereolithography and holographic data storage media [1].

In recent years, photoinitiated cationic polymerization had received revitalized interest due to its advantages such as various monomers and prepolymers [2,3], oxygen inhibition resistance [4], “living” polymerization [5,6], and the low operating temperatures, possibility of solvent-free process and short access times resulting in efficient reaction rate [7].

There are ionic and nonionic cationic photoinitiator on the basis of the molecular structure. The most commonly used ionic cationic photoinitiators employed for photoinduced cationic polymerizations are diaryliodonium, triarylsulfonium and ferrocenium salts [8,9]. Typical nonionic cationic photoinitiator includes triazine compounds, sulfonate compounds and disulfone compounds. α -Disulfone cationic photoinitiator is a kind of nonionic cationic photoinitiator with many advantages, such as high thermal stability, almost no volatile and good solubility. Wang and coworkers [10], found that α -disulfone compounds are soluble in common organic solvents such as acetone, 1,4-dioxane, and glycol ether and

the thermal decomposition temperatures of α -disulfone cationic photoinitiator was more than 190 °C. Quantum yield in solution was in the range of 0.4–0.6 with low pressure Hg lamp as exposure light source.

Vinyl ether is an attractive alternative to acrylates due to its low toxicity, odorless property and high reactivity. Under UV irradiation vinyl ethers exhibit higher curing rate than epoxides for the electron rich C=C bond and the stabilization by resonance of the carbocation [11,12]. In this study, photopolymerization kinetics of 4-tolyl methyl disulfone was studied by real-time infrared spectroscopy (FT-IR). The results indicated that 4-tolyl methyl disulfone is an effective cationic photoinitiator.

2. Experimental

2.1. Materials

4-Tolyl methyl disulfone (TMDS) was synthesized by the oxidation of disulfonyl hydrazine using concentrated nitric acid as oxidant. 4-Hydroxy butyl vinyl ether (HBVE) was purchased from Acros Organics. Diethylene glycol monovinyl ether (DEGMVE) was purchased from Tokyo Kasei. Hydroxyethyl vinyl ether (HVE) was purchased from J&K Chemical. Triethylene glycol divinyl ether (DVE-3) and 1,4-butanediol divinyl ether (BDDVE) were purchased from BASF SE. Isobutyl vinyl ether (IBVE), butyl vinyl ether (n-BVE) and ethyl vinyl ether (EVE) were purchased from Yi Li Biotechnology Co. (Shanghai, China).

The structures of 4-tolyl methyl disulfone cationic photoinitiator and eight vinyl ether monomers were shown in Fig. 1.

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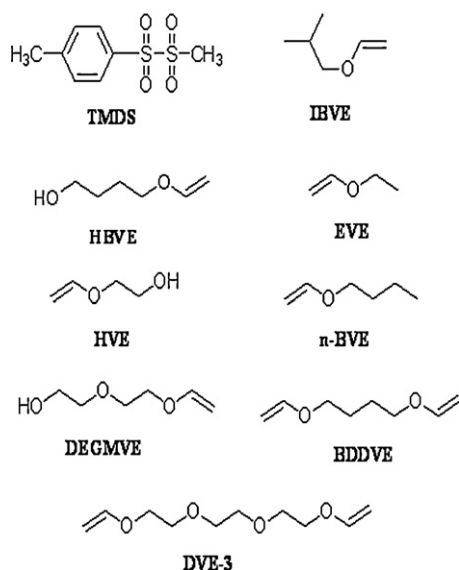


Fig. 1. Chemical structure of 4-tolyl methyl disulfone cationic photoinitiator and eight vinyl ether monomers.

2.2. Instrumentations

^1H NMR spectrum was recorded on a Bruker AV600 unity spectrometer operated at 600 MHz using TMS as an internal reference, with CDCl_3 as the solvent.

UV–vis absorption spectrum was recorded in ethanol solution on a Hitachi U-3010 UV–Vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). A cell path length of 1 cm was employed.

FT-IR spectrum was recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA, USA) equipped with an extended range KBr beam splitter and on MCT/A detector.

UV spot source was EFOS Lite with UV wavelength range of 220–500 nm (50 W miniature arc lamp, with 5 mm crystal optical fiber, Canada).

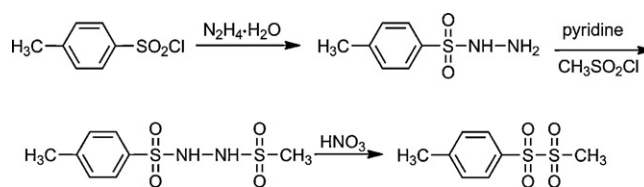
LC–MS (Ultra Performance LCTM/Quattro Premier XE which used T-wave ion transmission technology with ESI, APCI and ESCI as ion source, U.S. waters Company) used methanol or acetonitrile respectively as mobile phase.

2.3. Synthesis of TMDS [10]

When the temperature was lowered to 5 °C in ice-water bath, p-toluenesulfonyl chloride (9.5 g) was added slowly to hydrazine hydrate (9 mL, 80%) which was mixed with water (16 mL). After stirring for 5 h at room temperature, the reaction mixture was poured into cold water (25 mL). Then p-toluenesulfonyl hydrazide was collected after filtered off and washed with ether three times.

Methyl sulfonylchloride (50 mL) was added dropwise into mixture of p-toluenesulfonyl hydrazide (100 g) and anhydrous pyridine (150 mL) under ice bath at 0 °C and stirred for 2 h. The reaction mixture was poured into cold water (300 mL) and yellow solid was precipitated. Recrystallization from anhydrous ethanol gave N-methyl-N'-(p-methylphenyl) hydrazine.

Concentrated nitric acid (90 mL) was added dropwise slowly into N-methyl-N'-(p-methylphenyl) hydrazine (132 g) and the solution was stirred for 3.5 h at 20–25 °C. Cold water (250 mL) was added and kept stirring for 4 h at the room temperature. White solid was filtered off and washed with saturated aqueous solution of sodium hydrogen carbonate and water until the pH 7.0. Then it was dissolved in acetone and was precipitated after water was



Scheme 1. The synthesis route of TMDS.

added to. It was recrystallized from anhydrous ethanol two times to get TMDS. The reaction is shown in Scheme 1.

2.4. Photoreduction

The photoreduction of TMDS was studied by UV absorption spectroscopy. The TMDS were dissolved in ethanol. The relative rate of photoreduction was measured by the decrease in the maximal absorbance with irradiation time. The rate of TMDS disappearing (R_d) was calculated according to the following equation: [13,14]

$$R_d = \frac{-\delta[\text{TMDS}]}{\delta t} = - \left(\frac{[\text{TMDS}]}{A_{b0}} \right) \frac{\delta[A_b]}{\delta t} \quad (1)$$

A_{b0} is the maximal absorbance of TMDS before exposure to UV light.

2.5. Real-time infrared spectroscopy

The initiation efficiency of TMDS was studied by FT-IR. The mixture of volatile HBVE, HVE, DEGMVE, n-BVE, IBVE and EVE, with TMDS was placed in a mold made from glass slides and spacers; with 15 mm in diameter and 1.2 mm in thickness. It is well known that glass slides absorb the ultraviolet light strongly between 50 nm and 300 nm, which may reduce the UV absorption of TMDS to affect polymerization rate and the ultimate conversion. For BDDVE and DVE-3, the mixture of monomer with TMDS was applied between two pieces of KBr crystals. A series of RT-IR spectra were collected to determine the conversion of vinyl ether double bond. Upon irradiation, the decrease of the $=\text{C}-\text{H}$ absorption peak area from 780 to 865 cm^{-1} accurately reflects the extent of the polymerization.

For each sample, the series RT-IR were repeated three times. After baseline correction, conversion of the functional groups could be calculated by measuring the peak area at each time of the reaction and determined as following:

$$\text{DC} (\%) = \frac{(A_0 - A_t)}{A_0} \times 100 \quad (2)$$

where DC is the degree of vinyl ether double bond conversion at t time, A_0 is the initial peak area before irradiation, and A_t is the peak area of the double bonds at time t .

3. Results and discussion

3.1. Synthesis of TMDS

TMDS was synthesized according to Scheme 1. The preparation of hydrazide was carried out in water with simple post-processing and high yield. It is important to control the temperature in ice-salt bath because the preparation of dihydrazide and TMDS was violent and exothermic for the presence of pyridine and the oxidation agent of concentrated nitric acid. Recrystallization method was used to remove the residual pyridine which could affect the oxidative step to ensure the purity of dihydrazide. After the oxidative step, recrystallization method was used again to get pure TMDS. TMDS was identified by IR and ^1H NMR (Fig. 2).

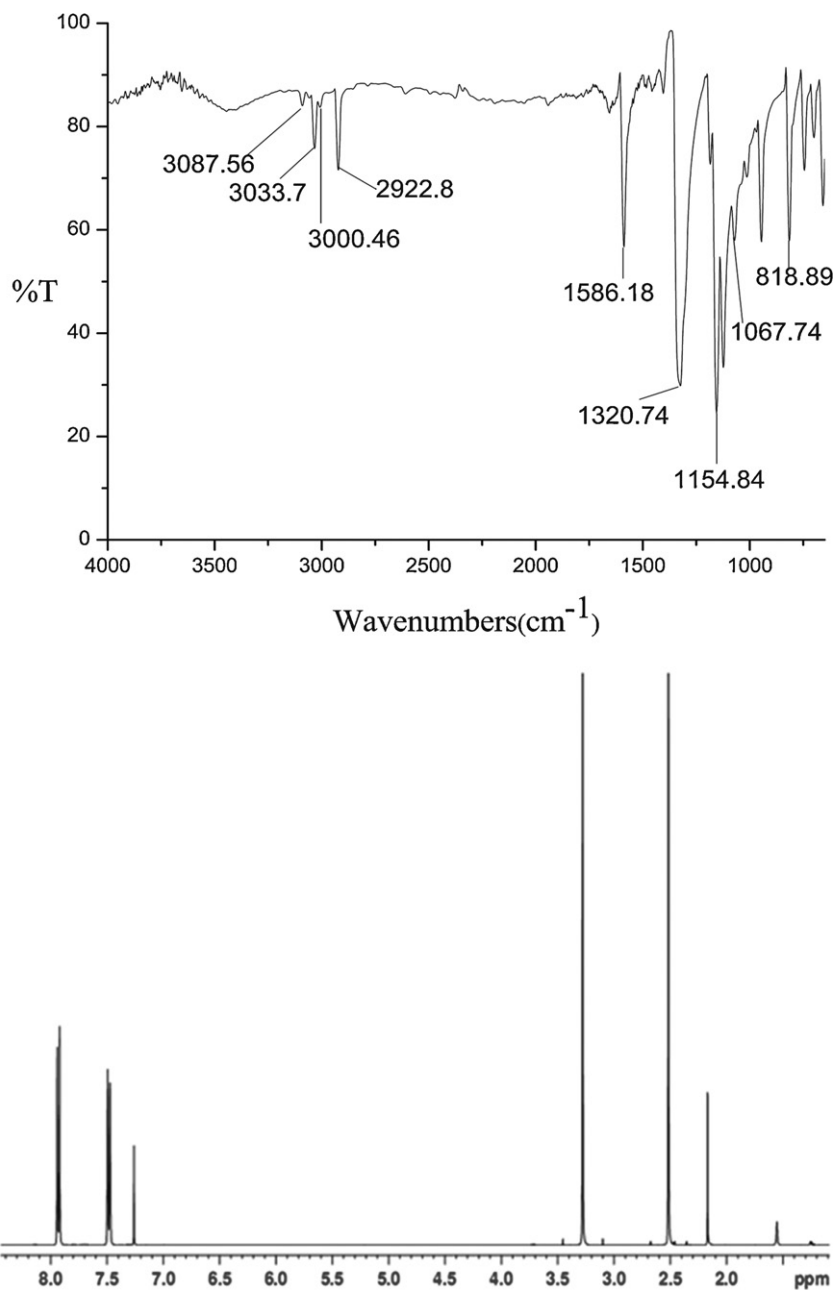


Fig. 2. The IR and ^1H NMR spectra of TMDS.

IR (cm^{-1}): 3087.56, 3033.7, 3000.46, 2922.8 ($\nu_{\text{ArC-H}}$), 1586 ($\nu_{\text{ArC=C}}$), 1320.74, 1154.84 ($\nu_{\text{O=S=O}}$).

^1H NMR: δ (400 MHz): 2.5 (s, 3H, CH_3), 3.3 (s, 3H, CH_3), 7.5 (d, 2H, ArH), 7.9 (d, 2H, ArH).

3.2. UV-vis absorption spectrum of TMDS

UV-vis absorption spectrum of TMDS and photodegradation study of TMDS in ethanol under UV irradiation in the region of 220–500 nm were showed in Fig. 3. It indicated that TMDS possesses a maximal absorption of 237 nm due to $\pi-\pi^*$ transition and molar extinction coefficient ϵ_{max} was $2.73 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

During the UV irradiation, the absorption band of TMDS in the range of 220–300 nm decreased significantly, and the decrease was

proportional to the irradiation time. According to Eq. (1), the calculated results of R_d was $1.616 \times 10^{-8} \text{ mol L}^{-1} \text{ S}^{-1}$.

It was generally accepted that the UV light irradiation led to homolysis of s-s and the formation of sub-sulfonic acids which could induce the polymerization of vinyl ether monomers. The process of photolysis is shown in Scheme 2.

3.3. LCMS analysis

LCMS was used to investigate the photodegradation products of TMDS. According to Scheme 2, TMDS could be photolyzed to form 4-methylbenzene sulfinic acid and methane sulfinic acid. TMDS could not be photolyzed in acetonitrile under UV light because there is no abstractable active hydrogen. While the hydrogen of the hydroxyl group of methanol was reactive. Fig. 4 showed that photodegradation occurred in methanol. TMDS, residual after photodegradation

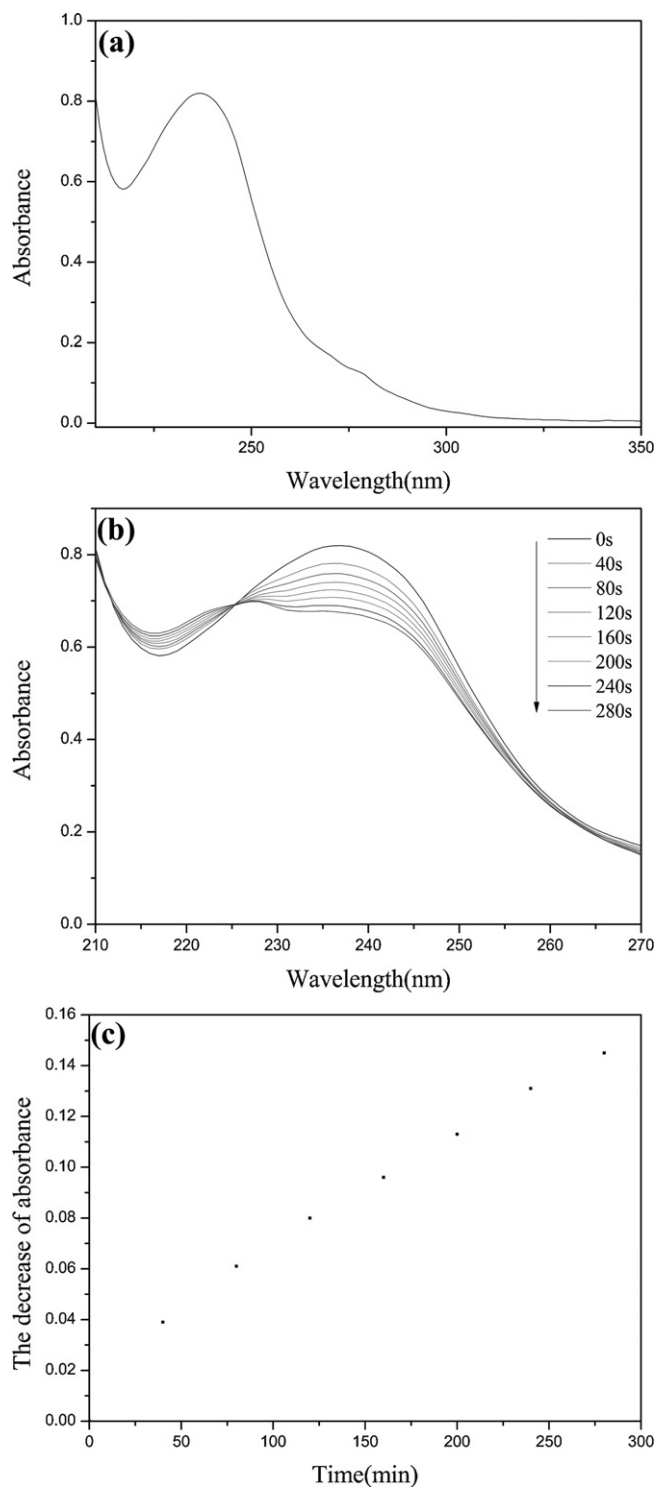
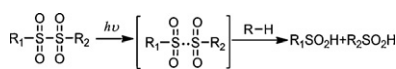


Fig. 3. (a) UV-vis absorption spectrum of TMDS, (b) photodegradation of TMDS in ethanol solution, and (c) the kinetics of the disappearance of TMDS absorption at 273 nm in ethanol ($[TMDS] = 3 \times 10^{-5}$ mol/L; light intensity = 50 mW/cm²).



Scheme 2. The photolysis process of TMDS.

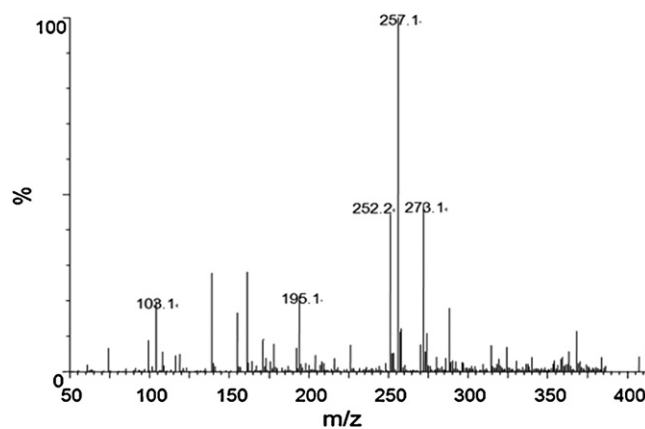


Fig. 4. LCMS chromatogram of TMDS in methanol, acquired in the positive-ion mode.

displayed $[M+H+Na]^+$ at a m/z of 257.1. Methane sulfinic acid displayed $[M+H+Na]^+$ at a m/z of 103.1 and 4-methylbenzene sulfinic acid displayed $[M+H+K]^+$ at a m/z of 195.1.

3.4. Effect of concentration of TMDS on photopolymerization kinetics

During UV irradiation, TMDS could photolysis to generate sub-sulfonic acids, which could induce the polymerization of vinyl ether double bond. Table 1 showed FT-IR data such as the maximum rate of polymerization (R_{pmax}), double-bond conversion (DC) for the photopolymerization of all the vinyl ether monomers that were investigated in this study.

Fig. 5 showed the conversion versus time plots of EVE, n-BVE and IBVE. 40 wt% of ethyl acetate was used as solvent because TMDS had lower solubility in EVE, n-BVE and IBVE. It showed that the polymerization rate and ultimate conversion increased with the increase of concentration of TMDS. Because the higher TMDS concentration, the more sub-sulfonic acids could generate during irradiation, which caused the higher rate of polymerization and ultimate conversion. From the data in Table 1 it is clear that EVE has the highest polymerization rate and the shortest time to reach ultimate conversion among the three volatile monomers EVE, n-BVE and IBVE may due to more double bond and the short chain which make it easy for the monomers to movement.

Fig. 6 illustrated the conversion versus time plots of HBVE, HVE and DEGMVE. At low TMDS concentration, a similar trend that the photopolymerization rate and ultimate conversion for vinyl ether monomers with hydroxyl tends to increase as the amount of the TMDS increases is observed in this study as in Fig. 5. It is for the same reason that higher TMDS concentration could generate more sub-sulfonic acids during irradiation and resulted in higher rate of polymerization and ultimate conversion. Fig. 6(b) also showed that as TMDS concentration is increased, the initial rate of polymerization increases and a larger number of polymer chains are initiated

Table 1

FT-IR data for photopolymerization of vinyl ether monomers initiated by 5 wt% TMDS with light intensity of 80 mW/cm².

Vinyl ether monomer	R_{pmax} (min ⁻¹)	T_{Rpmax} (min)	DC $_{Rpmax}$ (%)	T (min)	DC (%)
n-BVE	1.25	2.62	42.7	9.52	99.6
IBVE	1.09	2.19	36.1	5.90	99.6
EVE	1.27	2.52	50.7	5.02	96.8
HBVE	1.05	2.13	26.2	8.54	97.6
HVE	2.10	2.28	64.0	3.45	98.2
DEGMVE	1.16	1.79	30.3	6.98	98.2
BDDVE	1.68	3.08	48.3	4.45	96.5
DVE-3	9.24	0.50	40.3	1.05	87.6

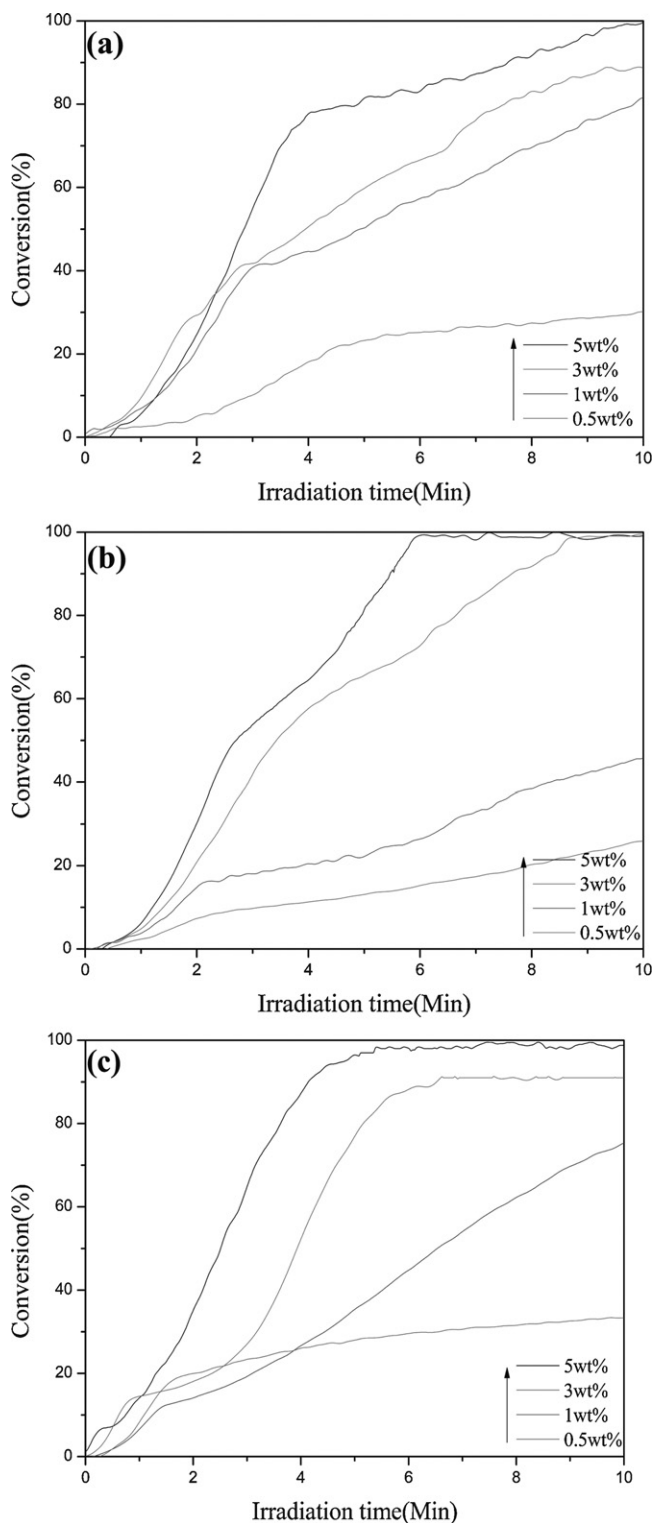


Fig. 5. Effect of TMDS concentration on the polymerization of vinyl ether monomers, 40 wt% ethyl acetate as solvent. (a) n-BVE, (b) IBVE, and (c) EVE (light intensity = 80 mW/cm²).

while ultimate conversion approaches the same value. A comparison of R_{pmax} and T values (Table 1) clearly demonstrates that HVE is more reactive among the three volatile vinyl ether monomers due to the same reason as EVE.

Higher R_{pmax} values and shorter time (T) to reach ultimate conversion of HBVE, HVE and DEGMVE with hydroxyl than that of EVE, n-BVE and IBVE were observed in Table 1. According to reports on

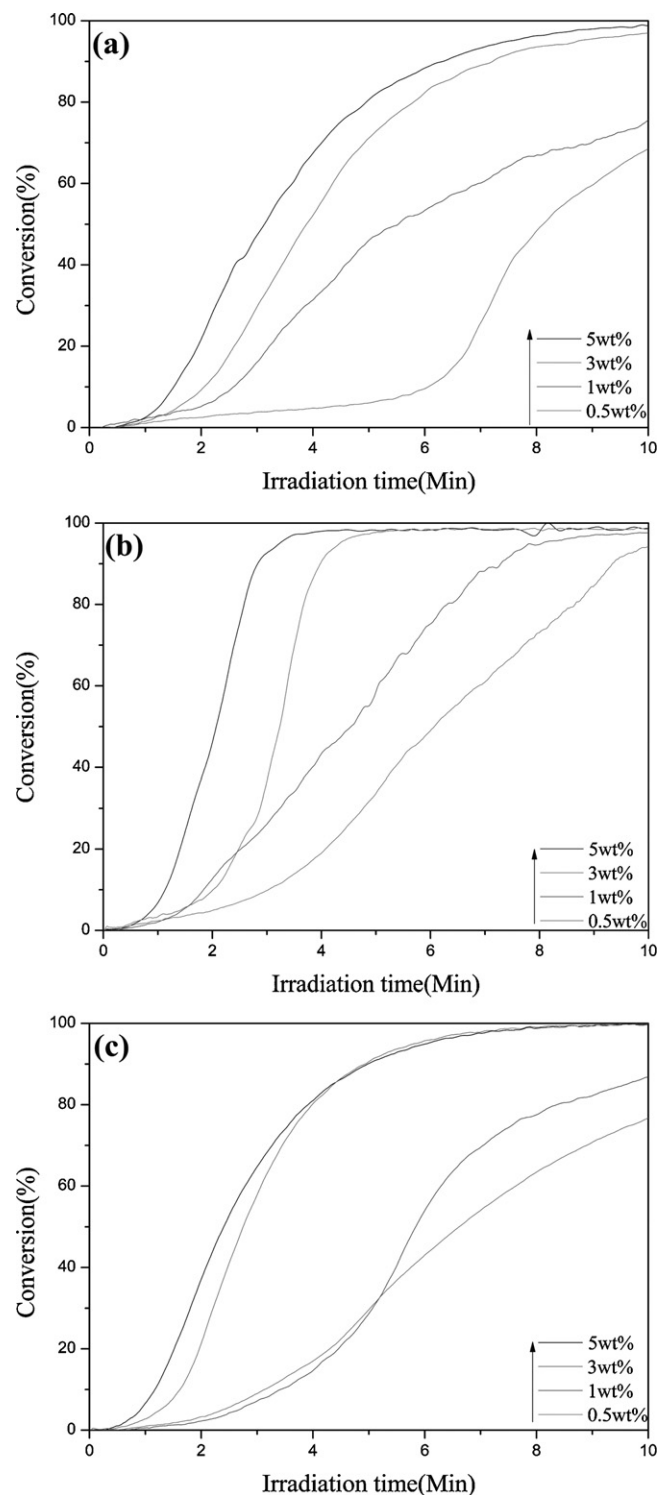


Fig. 6. Effect of TMDS concentration on the polymerization of vinyl ether monomers with hydroxyl. (a) HBVE, (b) HVE, and (c) DEGMVE (light intensity = 80 mW/cm²).

the photopolymerization of vinyl ether monomers with hydroxyl, it showed that chain transfer involving hydroxyl group occurs in cationic photopolymerization, the cationic photopolymerization proceeds more quickly for the vinyl ether monomer without hydroxyl groups [15]. We suggest that ethyl acetate in system of EVE, n-BVE and IBVE which could cut of UV source at about 256 nm is the main reason for the observation. This effectively reduces the initial concentration of TMDS available for polymerization of EVE, n-BVE and IBVE, hence, photopolymerization of these monomers is

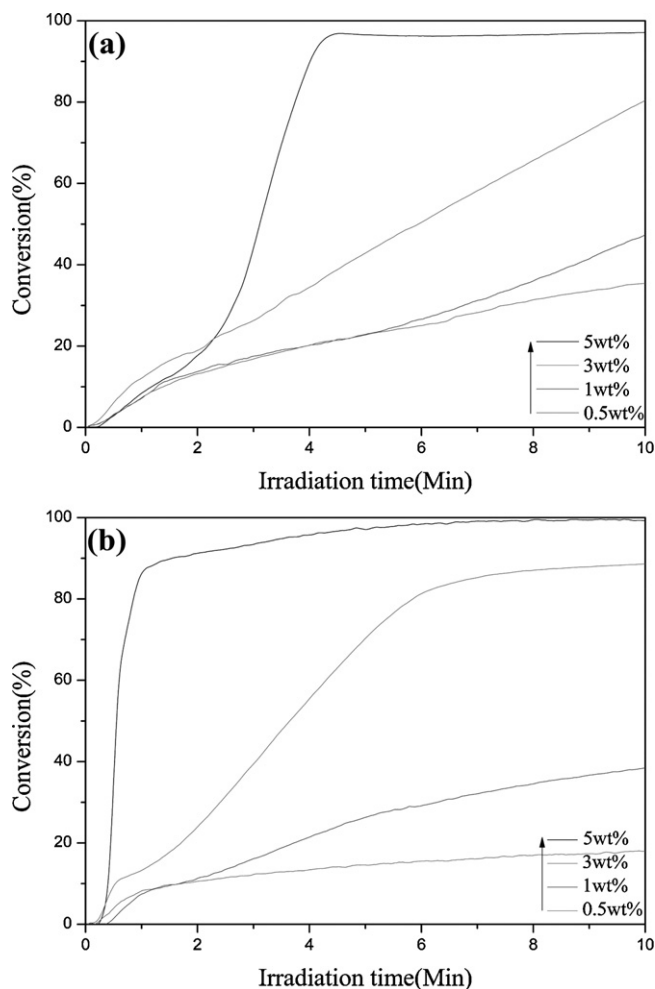


Fig. 7. Effect of TMDS concentration on the polymerization of divinyl ether monomers. (a) BDDVE and (b) DVE-3 (light intensity = 80 mW/cm²).

slow. As a result, the rate of polymerization and ultimate conversion are also reduced in these monomers.

Low volatile divinyl ether monomers BDDVE and DVE-3 were widely used in photopolymerization. The effect of variation in TMDS concentration on photopolymerization of divinyl ether monomers was studied and the results are shown in Fig. 7. It showed that the polymerization rate and ultimate conversion increased with the concentration of TMDS increased. BDDVE and DVE-3 both had high ultimate conversion and photopolymerization rate for that divinyl ether monomers have more vinyl ether double bond =C–H which led to high rate of polymerization and ultimate conversion. Table 1 showed that DVE-3 has the highest polymerization rate, which consistent with the reports [16] that in vinyl ether homopolymerization, based on exotherm peak maximum time, DVE-3 has the highest relative reactivity among eight mono-, di-, tri-, contained oxirane functionality and contained a hydroxyl group vinyl ether monomers.

3.5. Effect of light intensity on photopolymerization kinetics

Light intensity is another important factor to influence the kinetics that could not be ignored. Fig. 8 showed the conversion versus time plots of HBVE, HVE and DEGMVE initiated by 5wt% TMDS at different light intensity. Light intensity also played a vital role in determining the rate of the polymerization and ultimate conversion. The polymerization rate and ultimate conversion increased with increase of light intensity. It is also apparent that

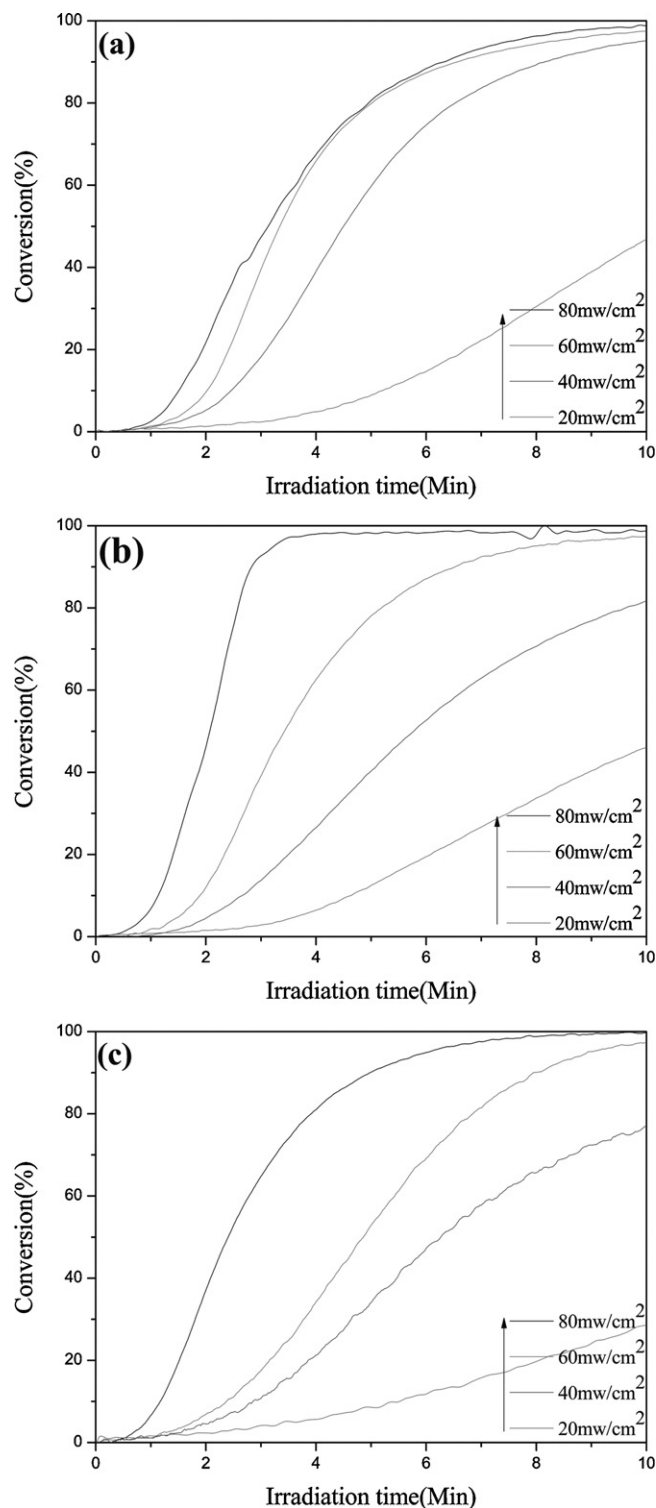


Fig. 8. Effect of light intensity on polymerization of volatile vinyl ether monomers, (a) HBVE, (b) HVE, and (c) DEGMVE (TMDS concentration = 5 wt%).

the contribution of the higher light intensity which could generate more sub-sulfonic acids to the increase in polymerization rate and ultimate conversion. HVE has higher polymerization rate and ultimate conversion than HBVE and DEGMVE.

The effect of light intensity on the polymerization of BDDVE and DVE-3 initiated by 5wt% TMDS was showed in Fig. 9. It has similar trend of effect of light intensity on the photopolymerization of volatile vinyl ether monomers. At low light intensity,

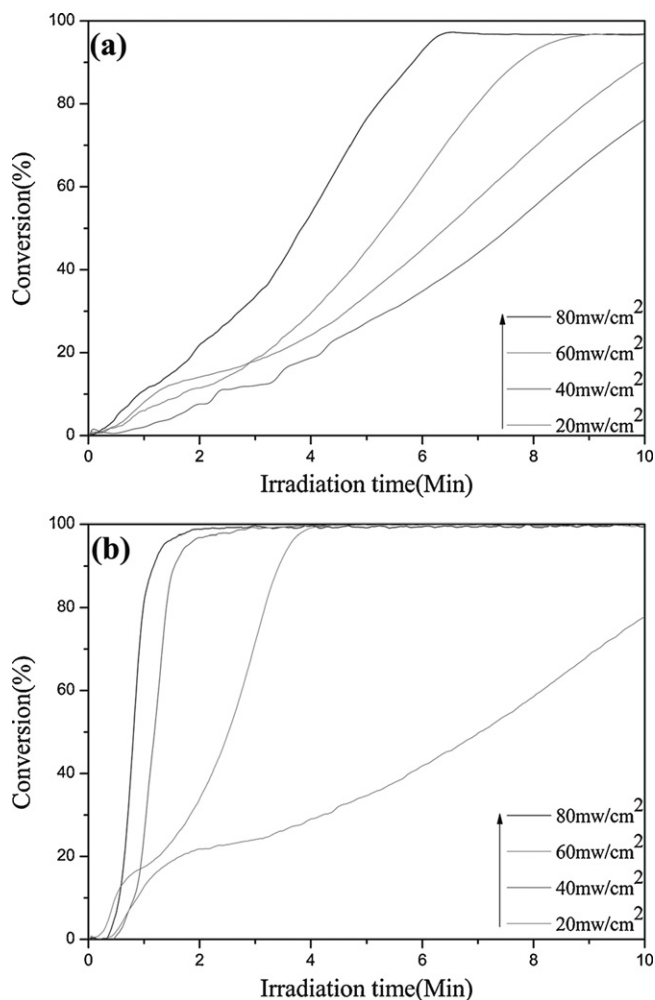


Fig. 9. Effect of light intensity on the polymerization of nonvolatile vinyl ether monomers. (a) BDDVE and (b) DVE-3 (TMDS concentration = 5 wt%).

the polymerization rate and ultimate conversion increased with increase in light intensity as more sub-sulfonic acids led to the increase in polymerization rate and ultimate conversion. When the light intensity was high enough, light intensity had no obvious influence on the ultimate conversion. However, the time to reach the ultimate conversion and the highest curing rate was shortened as the light intensity increased. The divinyl ether monomers DVE-3 and BDDVE had higher polymerization rate and ultimate conversion than that of volatile monovinyl ether monomers and vinyl ether monomers with hydroxyl.

4. Conclusions

TMDS was synthesized and its structure was confirmed by ^1H NMR and IR. It has a maximal absorption of 237 nm in ethanol due to $\pi-\pi^*$ transition with $\varepsilon_{\text{max}} = 2.73 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. LCMS showed that TMDS could be photolyzed in methanol to form sub-sulfonic acids under UV light. The kinetics data results showed that TMDS was an effective cationic photoinitiator. Both rate of polymerization and ultimate conversion was increased with increase in TMDS concentration and light intensity.

Acknowledgements

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